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(54) ELECTROLYTIC SOLUTION FOR LITHIUM SECONDARY BATTERY AND LITHIUM SECONDARY BATTERY USING SAME

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a lithium secondary battery excellent in battery characteristics such as cycle characteristics, electrical capacity, and preservation characteristics of the battery.

SOLUTION: As this electrolytic solution for a lithium secondary battery, an electrolytic solution having an electrolyte dissolved in a nonaqueous solvent is provided that contains a vinyl sulfone derivative expressed by the following general formula, (where, R is an alkyl group having the number of carbon atoms of 1 to 12, an alkenyl group having the number of carbon atoms of 1 to 12, or a cycloalkyl group having the number of carbon atoms of 3 to 6.), and a lithium secondary battery using this is also provided.



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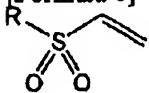
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CLAIMS

[Claim(s)]

[Claim 1] It sets to the electrolytic solution by which the electrolyte is dissolved in the non-aqueous solvent, and is the following general formula (I) in this electrolytic solution.

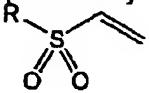
[Formula 1]



(-- R shows the alkyl group of carbon numbers 1-12, the ARUKENIRU machine of carbon numbers 1-12, and the cycloalkyl machine of carbon numbers 3-6 among a formula The electrolytic solution for lithium secondary batteries characterized by the vinyl sulfone derivative expressed with) containing.

[Claim 2] It sets to the lithium secondary battery which consists of the electrolytic solution by which the electrolyte is dissolved in the positive electrode, the negative electrode, and the non-aqueous solvent, and is the following general formula (I) in this electrolytic solution.

[Formula 2]



(-- R shows the alkyl group of carbon numbers 1-12, the ARUKENIRU machine of carbon numbers 1-12, and the cycloalkyl machine of carbon numbers 3-6 among a formula Lithium secondary battery characterized by the vinyl sulfone derivative expressed with) containing.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the new electrolytic solution for lithium secondary batteries which can offer the lithium secondary battery excellent also in cell properties, such as the cycle property of a cell, and electric capacity, a preservation property, and the lithium secondary battery using it.

[0002]

[Description of the Prior Art] In recent years, the lithium secondary battery is widely used as power supplies for a drive, such as small electronic equipment. The lithium secondary battery mainly consists of a positive electrode, nonaqueous electrolyte, and a negative electrode, and the lithium secondary battery which made lithium multiple oxides, such as LiCoO₂, the positive electrode, and used the carbon material or the lithium metal as the negative electrode is used especially suitably. And as the electrolytic solution for the lithium secondary batteries, carbonate, such as ethylene carbonate (EC) and propylene carbonate (PC), is used suitably.

[0003]

[Problem(s) to be Solved by the Invention] However, the rechargeable battery which has the further excellent property about cell properties, such as the cycle property of a cell and electric capacity, is called for. As a negative electrode, exfoliation of a carbon material is observed and according to the grade of a phenomenon, lithium secondary batteries using the high-crystallized carbon material, such as a natural graphite and an artificial graphite, have a bird clapper as capacity is irreversible. This exfoliation takes place, when the solvent in the electrolytic solution decomposes at the time of charge, and it originates in the electrochemical reduction of the solvent in the interface of a carbon material and the electrolytic solution. Although PC with the low melting point and a dielectric constant high especially had high electric conduction also in low temperature, when a graphite negative electrode was used, disassembly of PC took place and the trouble that it could not be used was in lithium secondary batteries. While EC also repeats charge and discharge, a solution happens in part, and cell performance degradation happens. For this reason, the present condition is that cell properties, such as the cycle property of a cell and electric capacity, are not necessarily satisfactory.

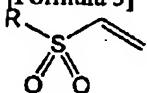
[0004] this invention aims at offering the electrolytic solution for lithium secondary batteries which can constitute the lithium secondary battery which solved the technical problem about the above electrolytic solutions for lithium secondary batteries, was excellent in the cycle property of a cell, and was further excellent also in cell properties, such as electric capacity and a preservation property in a charge state, and the lithium secondary battery using it.

[0005]

[Means for Solving the Problem] It sets to the electrolytic solution by which the electrolyte is dissolved in the non-aqueous solvent, and this invention is the following general formula (I) in this electrolytic solution.

[0006]

[Formula 3]



[0007] (R shows the alkyl group of carbon numbers 1-12, the ARUKENIRU machine of carbon numbers 1-12, and the cycloalkyl machine of carbon numbers 3-6 among a formula It is related with the electrolytic solution for lithium secondary batteries characterized by the vinyl sulfone derivative expressed with) containing.

[0008] It sets to the lithium secondary battery which consists of the electrolytic solution by which the electrolyte is dissolved in the positive electrode, the negative electrode, and the non-aqueous solvent, and is the following general formula (I) in this electrolytic solution.

[0009]
[Formula 4]

$$\begin{array}{c} \text{R} \\ | \\ \text{S} \\ || \\ \text{O} \quad \text{O} \\ | \\ \text{C=C} \end{array}$$

[0010] (-- R shows the alkyl group of carbon numbers 1-12, the ARUKENIRU machine of carbon numbers 1-12, and the cycloalkyl machine of carbon numbers 3-6 among a formula It is related with the lithium secondary battery characterized by the vinyl sulfone derivative expressed with) containing.

[0011] It is thought that the aforementioned vinyl sulfone derivative contained in the electrolytic solution has the effect which suppresses decomposition of the electrolytic solution, without covering with a passive-state coat the carbon material which contributed to passive-state coat formation in a carbon-material front face, and was high-crystallized in activity, such as a natural graphite and an artificial graphite, and spoiling the normal reaction of a cell.

[0012] [Embodiments of the Invention] In the compound contained in the electrolytic solution by which the electrolyte is dissolved in the non-aqueous solvent, R in the vinyl sulfone derivative expressed with the aforementioned formula (I) has a methyl group, an ethyl group, and the desirable alkyl group of carbon numbers 1-12 like a propyl group. A branching alkyl group like an isopropyl machine and an isobutyl machine is sufficient as an alkyl group. Moreover, the cycloalkyl machine of carbon numbers 3-6 like a vinyl group, an ARUKENIRU machine like an allyl group and a cyclo propyl group, and a cyclohexyl machine may be used.

[0013] As an example of a vinyl sulfone derivative expressed with the aforementioned formula (I), a divinyl sulfone [R= vinyl group], an ethyl vinyl sulfone [R= ethyl group], an isopropyl vinyl sulfone [R= isopropyl machine], a cyclohexyl vinyl sulfone [R= cyclohexyl machine], etc. are mentioned, for example.

[0014] If too few [when many / too /, the electric conductivity of the electrolytic solution etc. may change and a cell performance may fall, and], since the cell performance which sufficient coat was not formed but was expected will not be obtained, the content of a vinyl sulfone derivative expressed with the aforementioned formula (I) when adding the aforementioned vinyl sulfone derivative has 0.1 - 10% of the weight of an especially desirable range 0.01 to 20% of the weight to the weight of the electrolytic solution.

[0015] As a non-aqueous solvent used by this invention, what consists of a high dielectric constant solvent and a hypoviscosity solvent is desirable. As a high dielectric constant solvent, annular carbonate, such as ethylene carbonate (EC), propylene carbonate (PC), and butylene carbonate (BC), is mentioned suitably, for example. These high dielectric constant solvents may be used by one kind, and you may use them, combining them two or more kinds.

[0016] As a hypoviscosity solvent, amides, such as ester, such as nitril, such as lactone, such as ether, such as chain-like carbonate [, such as dimethyl carbonate (DMC), methylethyl carbonate (MEC), and diethyl carbonate (DEC),], tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 4-dioxane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, 1, and 2-dibutoxy ethane, and gamma-butyrolactone, and an acetonitrile, and a methyl propionate, and a dimethylformamide, are mentioned, for example. These hypoviscosity solvents may be used by one kind, and you may use them, combining them two or more kinds. A high dielectric constant solvent and a hypoviscosity solvent are chosen as arbitration, respectively, and are combined and used. in addition, an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent -- a capacity factor (high dielectric constant solvent : hypoviscosity solvent) -- usually -- 1:9-4:1 -- 1:4-7:3 come out comparatively preferably, and it is used

[0017] As an electrolyte used by this invention, LiPF6, LiBF4, LiClO4, LiN (SO2CF3)2, LiN (SO2C2F5)2, LiC (SO2CF3)3, etc. are mentioned, for example. These electrolytes may be used by one kind, and you may use them, combining them two or more kinds. 0.1-3 M of these electrolytes is usually preferably used by the concentration of 0.5-1.5M, dissolving in the aforementioned non-aqueous solvent.

[0018] The electrolytic solution of this invention is obtained by mixing an aforementioned high dielectric constant solvent and an aforementioned hypoviscosity solvent, dissolving the aforementioned electrolyte in this, and dissolving the vinyl sulfone derivative expressed with the aforementioned formula (I).

[0019] The electrolytic solution of this invention is suitably used as the composition member of a rechargeable battery, especially a composition member of a lithium secondary battery. Especially about composition members other than the electrolytic solution which constitutes a rechargeable battery, it is not limited but the various composition members currently used conventionally can be used.

[0020] For example, the compound metallic oxide of the at least one kind of metal and the lithium which are chosen from the group which consists of cobalt, manganese, nickel, chromium, iron, and vanadium as a positive-electrode

material (positive active material) is used. As such a compound metallic oxide, LiCoO₂, LiMn₂O₄, LiNiO₂, etc. are mentioned, for example.

[0021] the positive-electrode material of the above [a positive electrode] -- binders, such as electric conduction agents, such as acetylene black and carbon black, and a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), -- kneading -- a positive electrode -- after considering as a mixture, this positive-electrode material is rolled out to the foil and lath board of the aluminum as a charge collector, or the product made from stainless steel, and it is produced by heat-treating under a vacuum at the temperature of 50 degrees C - about 250 degrees C for about 2 hours

[0022] Matter, such as a carbon material [the pyrolytic carbons, the corks, the graphite, the organic high-molecular-compounds (artificial-graphite, natural graphite, etc.) combustion object, and the carbon fiber], a compound stannic-acid ghost, etc. which have the graphite-mold crystal structure which can emit [occlusion and] a lithium metal, a lithium alloy, and a lithium as a negative electrode (negative-electrode active material), is used. It is desirable to use the carbon material which has especially the graphite-mold crystal structure whose spacing (d002) of a lattice plane (002) is 3.35-3.40A. in addition, powder material like a carbon material -- binders, such as an ethylene-propylene-diene terpolymer (EPDM), a polytetrafluoroethylene (PTFE), and a polyvinylidene fluoride (PVDF), -- kneading -- a negative electrode -- it is used as a mixture

[0023] Especially the structure of a lithium secondary battery is not limited and the coin type cell which has the separator of a positive electrode, a negative electrode and a monolayer, or a double layer, a cylindrical cell, a square shape cell which has the separator of the shape of a positive electrode, a negative electrode, and a roll further, etc. are mentioned as an example. In addition, the fine porous membrane of a polyolefine well-known as separator, textile fabrics, a nonwoven fabric, etc. are used.

[0024]

[Example] Next, although an example and the example of comparison are given and this invention is explained concretely, these do not limit this invention at all.

After having prepared the non-aqueous solvent of example 1 [manufacture of the electrolytic solution] PC:DMC (capacity factor) = 1:2, having dissolved so that it might become the concentration of 1M about LiPF₆ at this, and preparing the electrolytic solution, the divinyl sulfone [R= vinyl group] was further added as an additive so that it might become 2.0 % of the weight to the electrolytic solution.

[0025] [Production of a lithium secondary battery and measurement of a cell property] Acetylene black (electric conduction agent) was mixed 10% of the weight 80% of the weight, the polyvinylidene fluoride (binder) was mixed for LiCoO₂ (positive active material) at 10% of the weight of a rate, N-methyl pyrrolidone was added to this, and it was made the shape of a slurry, and applied on aluminum foil. Then, pressing of this was dried and carried out and the positive electrode was prepared. The natural graphite (negative-electrode active material) was mixed 90% of the weight, the polyvinylidene fluoride (binder) was mixed at 10% of the weight of a rate, N-methyl pyrrolidone was added to this, and it was made the shape of a slurry, and applied on copper foil. Then, pressing of this was dried and carried out and the negative electrode was prepared. And using the separator of a polypropylene fine porosity film, the above-mentioned electrolytic solution was poured in and the coin cell (3.2mm in the diameter of 20mm, thickness) was produced. Using this coin cell, under the room temperature (20 degrees C), it charged to final-voltage 4.2V for 5 hours, and, next, discharged to final-voltage 2.7V under the 0.8mA constant current, and this charge and discharge were repeated by the 0.8mA constant current and the constant voltage. Initial charge-and-discharge capacity was almost equivalent to the case (example 2 of comparison) where EC-DMC (1/2) is used as the electrolytic solution, and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 86.1%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0026] When used the divinyl sulfone [R= vinyl group] 0.5% of the weight to the electrolytic solution as example 2 additive, and also the electrolytic solution was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 84.7%. The production conditions and cell property of a coin cell are shown in Table 1.

[0027] When used the divinyl sulfone [R= vinyl group] 8.0% of the weight to the electrolytic solution as example 3 additive, and also the electrolytic solution was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 81.1%. The production conditions and cell property of a coin cell are shown in Table 1.

[0028] When used the ethyl vinyl sulfone [R= ethyl group] 2.0% of the weight to the electrolytic solution as example 4 additive, and also the electrolytic solution was prepared like the example 1, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 85.7%. The production conditions

and cell property of a coin cell are shown in Table 1.

[0029] The non-aqueous solvent of example of comparison 1 PC:DMC(capacity factor)=1:2 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF₆ at this. At this time, the additive was not added at all. When the coin cell was produced like the example 1 using this electrolytic solution and the cell property was measured, disassembly of PC took place at the time of first time charge, and it has not discharged at all. As a result of disassembling and observing the cell after first time charge, exfoliation was accepted in the graphite negative electrode. The production conditions and cell property of a coin cell are shown in Table 1.

[0030] After having prepared the non-aqueous solvent of example 5 EC:DMC(capacity factor)=1:2, having dissolved so that it might become the concentration of 1M about LiPF₆ at this, and preparing the electrolytic solution, the divinyl sulfone [R= vinyl group] was further added as an additive so that it might become 2.0 % of the weight to the electrolytic solution. When the coin cell was produced like the example 1 using this electrolytic solution and the cell property was measured, initial charge-and-discharge capacity was almost equivalent to the case (example 2 of comparison) where only EC-DMC (1/2) is used as the electrolytic solution, and when the cell property after 50 cycles was measured, the service-capacity maintenance factor when making initial service capacity into 100% was 91.1%. Moreover, the low-temperature property was also good. The production conditions and cell property of a coin cell are shown in Table 1.

[0031] When used the ethyl vinyl sulfone [R= ethyl group] 2.0% of the weight to the electrolytic solution as example 6 additive, and used MEC instead of DMC, and also the electrolytic solution was prepared like the example 5, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 90.4%. The production conditions and cell property of a coin cell are shown in Table 1.

[0032] When replaced with LiCoO₂, used LiMn₂O₄ as example 7 positive active material, and used the divinyl sulfone [R= vinyl group] 3.0% of the weight to the electrolytic solution as an additive, and also the electrolytic solution was prepared like the example 5, the coin cell was produced and the cell property after 50 cycles was measured, the service-capacity maintenance factor was 89.3%. The production conditions and cell property of a coin cell are shown in Table 1.

[0033] The non-aqueous solvent of example of comparison 2 EC:DMC(capacity factor)=1:2 was prepared, and it dissolved so that it might become the concentration of 1M about LiPF₆ at this. At this time, the additive was not added at all. The coin cell was produced like the example 1 using this electrolytic solution, and the cell property was measured. The service-capacity maintenance factor after 50 cycles was 83.8% to initial service capacity. The production conditions and cell property of a coin cell are shown in Table 1.

[0034]

Table 1

	正極	負極	添加剤	追加量 wt%	電解液組成 (容量比)	50サイ クル放電 容量維持 率%
実施例 1	LiCoO ₂	天然墨鉛	ジビニル スルホン	2.0	1M LiPF ₆ PC/DMC=1/2	85.1
実施例 2	LiCoO ₂	天然墨鉛	ジビニル スルホン	0.5	1M LiPF ₆ PO/DMC=1/2	84.7
実施例 3	LiCoO ₂	天然墨鉛	ジビニル スルホン	8.0	1M LiPF ₆ PC/DMC=1/2	81.1
実施例 4	LiCoO ₂	天然墨鉛	エチルビ ニルスル ホン	2.0	1M LiPF ₆ PC/DMC=1/2	85.7
比較例 1	LiCoO ₂	天然墨鉛	なし	0.0	1M LiPF ₆ PC/DMC=1/2	充放電不 可
実施例 5	LiCoO ₂	天然墨鉛	ジビニル スルホン	2.0	1M LiPF ₆ EC/DMC=1/2	91.1
実施例 6	LiCoO ₂	天然墨鉛	エチルビ ニルスル ホン	2.0	1M LiPF ₆ EC/MEC=1/2	80.4
実施例 7	LiMn ₂ O ₄	天然墨鉛	ジビニル スルホン	3.0	1M LiPF ₆ EC/DMC=1/2	89.3
比較例 2	LiCoO ₂	天然墨鉛	なし	0.0	1M LiPF ₆ EC/DMC=1/2	83.8

[0035] In addition, this invention is not limited to the example of a publication, but various combination which can be guessed is easily possible for it from the meaning of invention. Especially the combination of the solvent of the above-mentioned example is not limited. Furthermore, although the above-mentioned example is related with a coin cell, this

invention is applied also to the cell of cylindrical shape and prism type.

[0036]

[Effect of the Invention] According to this invention, the lithium secondary battery excellent in cell properties, such as the cycle property of a cell, electric capacity, and a preservation property, can be offered.

[Translation done.]